

BIOLOGICALLY IMPORTANT COMPOUNDS IN SYNFUELS PROCESSES\*. B. R. Clark, C.-h. Ho, W. H. Griest, and M. R. Guerin. Analytical Chemistry Division, Oak Ridge National Laboratory, P. O. Box X, Oak Ridge, Tennessee 37830.

Crude products, by-products and wastes from synfuel processes contain a broad spectrum of chemical compounds--many of which are active in biological systems. Discerning which compound classes are most important is necessary in order to establish effective control over release or exposure. Polycyclic aromatic hydrocarbons (PAH), multi-alkylated PAH, primary aromatic amines and N-heterocyclic PAH are significant contributors to the overall mutagenic activities of a large number of materials examined. Ames test data show that the basic, primary aromatic amine fraction is the most active. PAHs, multi-alkylated PAHs and N-heterocyclic PAHs are all components of the neutral fraction. In nearly all cases, the neutral fractions contribute the largest portion of the mutagenic activity, while the basic primary aromatic amine fractions have the highest specific activity. Neutral fractions are usually the largest (wt%) whereas the total basic fractions are small by comparison; thus, the overall greater contribution of the neutral fraction to the mutagenic activity of most samples. Biologically active constituents are isolated in preparative scale amounts from complex mixtures utilizing combinations of liquid-liquid extraction and various liquid chromatographic column-eluent combinations. Fractions are characterized using a combination of spectroscopic techniques and gas chromatography/mass spectrometry. (\*Research sponsored by the Office of Health and Environmental Research, Department of Energy, under contract W-7405-eng-26 with the Union Carbide Corporation.)

THE ELEMENTAL COMPOSITION OF SHALE OILS. J. P. Fox. Energy and Environment Division, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720.

The abundance of 47 elements were measured in 12 shale oils from LETC's controlled-state retort, 7 shale oils from LLL's 125-kg simulated in-situ retort and in oils from the Geokinetics, Occidental, Equity and Paraho processes using neutron activation analysis, x-ray fluorescence spectrometry and Zeeman atomic absorption spectroscopy. The elements studied include C, H, N, As, Se, Co, Ni, Fe, Mn, Zn, U, Cl, Na and others. The resulting data were analyzed to determine the effect of retort operating conditions on measured elemental abundances.

This paper compares the elemental abundances in oils from simulated, surface and in situ processes in the framework of retort operating conditions and discusses the potential environmental implications of observed trace element patterns. This investigation indicates that the major elements in shale oils (>10 ppm) are C, H, N, S, Fe, As, Cl and Na. The elements Al, Ba, Co, Cr, Cu, Hg, Mg, Mn, Mo, Ni, Se, V and Zn occur at concentrations of from 0.1 ppm to less than 10 ppm. All other elements studied occurred at less than 0.1 ppm in most oils. Striking differences were observed between the elemental abundances of Antrim, Moroccan and Green River shale oils.

ANALYSIS OF ENERGY WASTE EFFLUENTS FOR ORGANIC CHEMICALS USING THE MASTER ANALYTICAL SCHEME. Linda Sheldon, Shirley Yung, Roger Wiseman, Larry Michael, and Edo Pellizzari  
Analytical Sciences Division, Chemistry and Life Sciences Group, Research Triangle  
Institute, P. O. Box 12194, Research Triangle Park, NC 27709.

A variety of analytical methods were tested during the development of a comprehensive scheme to identify and quantitate volatile organic chemicals in aqueous samples using high resolution gas chromatography/mass spectrometry/computer (GC/MS/COMP) as the major analytical tool. Volatile organics are defined as those compounds which will either elute from a GC column at 300°C in one hour or less or which may be derivatized to meet these criteria.

Highly volatile (bp <175°C), hydrophobic compounds were analyzed using a modified purge and trap procedure. Solvent extraction with pH adjustment served to concentrate the less volatile (bp >175°C) hydrophobic compounds. Ionic organics were concentrated by ion exchange, then chemically derivatized prior to gas chromatography. Lastly, volatile polar organics were concentrated by fractional distillation. As an alternative to direct aqueous injection, the distillate was injected onto a Tenax GC precolumn through a heated injection port, the water vented, and the organics were thermally desorbed into a gas chromatograph. For energy waste effluents, methods which gave a minimum detection limit of 10 ppb with 40% recovery were considered acceptable.

Developed methods were tested on a variety of spiked and unspiked sample waters including energy waste effluents. Specific problems with this sample matrix and test results will be presented. This research was supported by EPA Contract No. 68-03-2704.

TRACE ELEMENT BEHAVIOR IN THE SOLVENT REFINED COAL PROCESSES. R. H. Filby, S. R. Khalil,\* and M. L. Hunt. Nuclear Radiation Center, Washington State University, Pullman, Washington 99164.

High sulfur coals contain significant quantities of trace metals which may have undesirable effects on liquefaction processes, on upgrading of derived syncrudes, or on the environment. A study of the fate of up to 35 trace elements in the SRC I and SRC II processes by neutron activation analysis (NAA) and atomic absorption spectroscopy (AAS) shows that significant emissions of toxic elements from the Fort Lewis, Washington 50 ton per day pilot plant (operated by Pittsburg & Midway Coal Mining Co.) occur and that, except for Hg in the SRC II process satisfactory material balances can be obtained for SRC I and SRC II processes. In the case of Hg in the SRC II process, and to a lesser extent As, Se and Sb, transport via gaseous streams has been demonstrated and can be related to the volatility and reactions of  $\text{Hg}^0$ ,  $\text{HgS}$ ,  $\text{H}_2\text{Se}$ ,  $\text{As}_4^0$ , etc. The NAA and AAS techniques and their application to the complex matrices encountered in coal liquefaction processes are discussed.

\*Presently at University of Kentucky

CHARACTERIZATION AND MUTAGENICITY OF SHALE OIL FRACTIONS, Deborah S. Sklarew, Donald M. Schoengold, Richard A. Pelroy<sup>†</sup>, Sylvia P. Downey, Barbara A. Vieux, James T. Crestot<sup>†</sup>, Physical Sciences Dept. and Biology Dept.<sup>†</sup>, Pacific Northwest Laboratory, operated for the Department of Energy by Battelle Memorial Institute

Product oils from several shale oil operations have been analyzed for organic compounds which are potential biological/environmental hazards. Two fractionation schemes have been compared both from an analytical and a biological point of view. The first method involves acid-base fractionation; the second uses partition chromatography on Sephadex LH-20. Fractions have been tested for mutagenicity in the Ames assay and those which gave positive results were further subdivided and analyzed by gas chromatography-mass spectrometry. In the case of the Sephadex LH-20 method, mutagenicity is concentrated in the methanol fractions; in the acid-base separation, mutagenicity is found in the basic and tar fractions.

# COMPARISON AND CONTRAST OF TRACE ELEMENTS IN CRUDE SHALE OILS AND PETROLEUM

C. L. Wilkerson, D. S. Sklarew, J. C. Evans and J. S. Fruchter, Pacific Northwest Laboratory, Richland, WA 99352

The abundances and chemical forms of a large group of elements including the trace metals As, Co, Fe, Mo, Ni, Se, V and Zn were determined in three whole and fractionated shale oils obtained from Colorado and Utah oil shale reserves. The crude shale oils were representative product oils from an above-ground, a modified in-situ, and a true in-situ retorting process and were produced by pilot plant or larger sized facilities. Elemental abundances were determined by several modern analytical techniques including instrumental neutron activation analysis, energy dispersive X-ray fluorescence analysis, prompt  $\gamma$ -ray activation analysis, and plasma emission spectrometry. The analyses were compared to identify major differences between elemental partitioning yields of the various retorting technologies and were further compared and contrasted with reported elemental concentrations in petroleum. The elements As and Fe were found to be the most prominent trace metals in the shale oil matrix and As and Se levels were observed to be 1 to 2 orders of magnitude greater than those reported for petroleum.

ENVIRONMENTAL ORGANIC CHEMISTRY: THE ISOLATION AND IDENTIFICATION OF ORGANIC AND ORGANOMETALLIC COMPOUNDS FROM OIL SHALE RETORT WATERS.\* Richard H. Fish and Mathilde J. Kland. Energy and Environment Division, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720.

The complex nature of the inorganic, organic and organometallic contaminants found in oil shale retort waters is important to elucidate in order to evaluate the potential problems connected with the release of these compounds to the environment.

Our efforts have focused on more clearly defining the organic and the organometallic species, either synthesized or released during the retorting process, that eventually end up in the retort waters. Retort waters from LLL and LETC simulated in situ retorts and from Occidental's Logan Wash experiments were extracted with methylene chloride and the components separated and analyzed by a combination of dry column, thin layer and high performance liquid chromatography as well as capillary gas chromatography-mass spectrometry and nuclear magnetic resonance spectroscopy.

A discussion of the classes of organic and organometallic species identified, together with some of their toxicological and environmental implications, will be presented.

• Studies supported through the Department of Energy under contract no. W-7405-ENG-48.

INTERLABORATORY COMPARISON OF ENVIRONMENTAL ANALYSES ASSOCIATED WITH SYN-FUEL PRODUCTION, W. E. May, J. M. Brown, S. N. Chesler, F. R. Guenther, H. S. Hertz, L. R. Hilpert, R. N. Parris, K. L. Ritchie, and S. A. Wise, Center for Analytical Chemistry, National Bureau of Standards, Washington, DC 20234

In order to begin evaluating the state-of-the-art of the determination of pollutants associated with the production of alternate fuels, seven collaborative studies have been conducted by NBS. The aim of the five initial studies was to ascertain how well participating laboratories could perform the final quantitation step in a trace organic analytical scheme. The materials examined in these initial studies were two polynuclear aromatic hydrocarbon in hexane samples, a phenols in water sample, a phenols in hexane sample and a N-heterocyclic compounds (azaarenes) in hexane sample. Each of these samples contained between five and eight pure compounds, with each compound being present at the 1-100  $\mu\text{g/mL}$  (ppm) level.

The last two collaborative studies involved quantitative analyses of selected phenols, polynuclear aromatic hydrocarbons and N-heterocyclics in a shale oil and a solvent refined coal (SRC) material. Such analyses usually required a minimum of three steps: (1) Isolation of the analyte from the sample matrix; (2) Separation of the analyte from non-analyte interference; (3) measurement of detector response for the analyte and relating that to the concentration of the analyte in the original sample. The results of these collaborative studies will be reported and discussed along with methodologies developed at NBS for certifying the concentration of selected phenols, PAH and N-heterocyclics in alternate fuels.



ANALYSIS OF SULFUR HETEROCYCLES IN COAL-DERIVED PRODUCTS AND SHALE OILS\* C. Willey  
M. Iwao, T. A. Broadbent, R. N. Castle, and M. L. Lee, Department of Chemistry,  
Brigham Young University, Provo, Utah 84602.

The carcinogenic activity demonstrated by complex mixtures of polycyclic aromatic compounds (PAC) has stimulated much effort by researchers to identify individual mixture components. Found in low concentrations among the mixture components of most PAC fractions from coal-derived products and shale oils are the sulfur heterocycles. Due to their low concentrations, an enrichment of the heterocyclic sulfur compounds is necessary for identification. A recently developed method to isolate the sulfur heterocycle fraction from a composite aromatic fraction has greatly aided efforts to separate and identify individual heterocyclic sulfur compounds by glass capillary gas chromatographic mass spectrometry.

In this study, the developed methodology for the enrichment and subsequent separation and identification of sulfur heterocycle fractions has been applied to selected coal gasification tars, coal liquids, and shale oils. Identification was accomplished through comparison of mass spectral and chromatographic retention data of mixture components with standard reference compounds.

Since few standard reference compounds of sulfur heterocycles are commercially available, compounds predicted by mass spectrometry to be present in enriched sulfur heterocycle fractions were synthesized. These compounds were used to obtain chromatographic retention data and for biological testing.

\*This study was supported by the U.S. Department of Energy, Division of Biomedical and Environmental Research, Contract No. DE-AC02-79EV10237.

ENVIRONMENTAL HEALTH AND SAFETY ASPECTS OF SYNFUELS PROCESSING--AN OVERVIEW. E. J. Salmon, National Academy of Sciences, 2101 Constitution Avenue, Washington DC 20418 and H. Perry, Resources for the Future, 1755 Massachusetts Ave. Washington, DC 20036.

OBSERVATIONS ON THE POTENTIAL ENVIRONMENTAL EFFECTS OF SYNFUELS PRODUCTION. T. K. Janes, Environmental Protection Agency, Research Triangle Park, NC 27711

ENVIRONMENTAL IMPACT OF THE FORMATION OF A SYNFUELS INDUSTRY. M. J. Reilly, ESCO,  
444 N. Capitol St. N. W. Washington DC 20001.

RISK ANALYSIS OF COAL UTILIZATION--SYNFUELS VS. DIRECT COMBUSTION. H. Inhaber,  
Atomic Energy Control Board, Ottawa, Canada KIP 559.

THE IMPACT OF "NO ACTION". J. G. Seay, Institute of Gas Technology, 3436 S. State St. Chicago IL 60616.

ENVIRONMENTAL CONSIDERATIONS IN COAL GASIFICATION PLANT DESIGN. R. J. Feldman,  
C. B. Fegnan and N. R. Passow, The Lummus Company, Division of Combustion Engi-  
neering, 1515 Broad St., Bloomfield NJ 07003.

ENVIRONMENTAL AND HEALTH ASPECTS OF COAL LIQUEFACTION PLANT DESIGN. C. R. Moxley  
Gulf Mineral Resources Company, 1720 S. Bellaire, Denver CO 80222



ASSESSMENT OF THE WATER BALANCE IN COAL CONVERSION PLANT DESIGN. H. Takash, C. S. Kelley and W. G. Atkins, H. Mittelhauser Co., 5120 Belmont Rd. Suite G, Downers Grove IL 60515.

TRANSPORTATION FUELS FROM SYNTHESIS GAS. R. H. Fischer and R. E. Hildebrand. U.S. Department of Energy, Office of Fossil Energy Programs, Division of Fossil Fuel Processing, Mail Stop E-338/Germantown, Washington, DC 20545.

#### ABSTRACT

The Department of Energy (DOE) has formulated a program to develop improved processes to convert synthesis gas from coal to quality transportation fuels. The program involves four elements.

1. Improved integration of gasification with liquefaction. This involves the use of low ratio  $H_2$  to CO synthesis gas in the hydrocarbon formation step. Low ratio  $H_2$  to CO can be converted to hydrocarbon by means of the Kolbel-Engelhardt reaction. The net result is considerable energy savings in steam.
2. Improved selectivity by use of shape selective catalyst. Normal Fischer-Tropsch reaction chemistry is subject to inherent limitations due to the chain growth mechanisms. Use of shape selective catalysts can result in circumvention of this limitation by the use of an intermediate that can be formed in high selectivity (methanol) or by inhibition of the chain growth mechanism.
3. Use of improved thermally efficient liquefaction reactors. Use of the liquid or slurry phase reactor can possibly result in single pass conversion, elimination of recycle, improved temperature control, and recovery of the heat of reaction at higher efficiency.
4. Production of methanol and fuel grade alcohol from low ratio  $H_2$ -CO syn gas using liquid or slurry phase reactors.

The key to success in this effort will be a close integration of the gasification and synthesis steps so that the amount of steam and oxygen consumed by the total process will be minimized and the thermal efficiency maximized.

The initial contracts in this program are about to be signed and others are beginning negotiation. The goals of the program and this up coming work will be discussed.